

# SCIENCE FOR CERAMIC PRODUCTION

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## INTENSIFICATION OF SINTERING OF CALCIUM-BEARING CERAMIC MIXTURES

N. D. Yatsenko,<sup>1</sup> N. A. Vil'bitskaya,<sup>1</sup> S. P. Golovanova,<sup>1</sup> A. P. Zubekhin,<sup>1</sup> and V. P. Rat'kova<sup>1</sup>

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The specifics of intensification of the sintering process in faience mixtures with an increased content of high-calcium waste were investigated upon introduction of various mineralizers. It was determined that sintering is intensified when the process mainly occurs in the solid phase with the RO : R<sub>2</sub>O ratio equal to 7–9.

The extensive use of technogenic materials which have some positive properties for the production of ceramics helps in solving a very important engineering problem, i.e., production of ceramics with good service parameters using available resource-saving technologies or technologies which are upgraded through increasing the production efficiency. This problem can be solved by selecting an optimum composition of mixture components, by controlling the sintering process through employing a necessary quantity of mineralizing additives, and by reducing the firing temperature.

It is known that traditionally the firing temperature can be decreased by introducing fluxes into ceramic mixtures. The effect of carbonate-bearing fluxes of the calcite type begins at a temperature above 1000°C, when the reaction of calcium oxide with other components of the mixture results in the formation of low-melting eutectics [1]. However, it is established that ceramic materials with required properties can be produced at temperatures below 1000°C with a certain quantity of calcium-bearing and alkaline components in the ceramic mixture.

The mixture contains clay, sand, high-calcium waste, R<sub>2</sub>O-containing materials (which can be nepheline-syenite, clay shale, polymetallic ore concentration waste, etc.) [2, 3]. Using up to 25 wt.% high-calcium waste in the presence of not more than 2% R<sub>2</sub>O makes it possible to make high-strength faience products, which are determined by their phase compositions, primarily, the presence of anorthite CaO · Al<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub>. The formation of this compound at a low firing temperature (950°C) proceeds in a rather complex way, in sintering which is fundamentally solid-phase, in the

presence of the optimum amount of the alkaline components. Any modification in the RO : R<sub>2</sub>O ratio inevitably deteriorates the mechanical strength of ceramics and leads to the formation of calcium silicates in addition to anorthite. Therefore, research in the field of sintering intensification, i.e., the formation of anorthite in calcium-containing ceramic mixtures due to various mineralizing additives, which makes possible the low-temperature firing of mixtures, is of clear scientific and practical interest.

In this case, it is necessary to determine the parameters (chemical, physicochemical, technological) which can direct the sintering process toward the formation of calcium aluminosilicate.

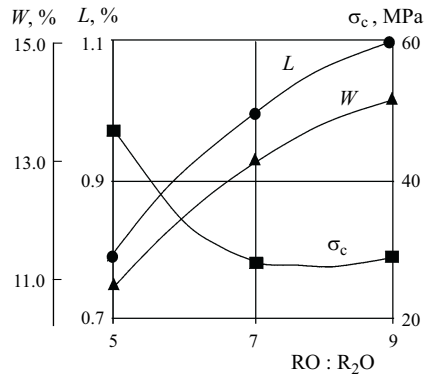
The investigated mixtures contained the known raw materials: Vladimirovskoe clay, Tarasovskoe sand, and high-calcium waste resulting from power plant sewage purification, and window glass cullet acted as the R<sub>2</sub>O-containing component. The latter is the strongest mineralizer, intensely destroying the silicon-oxygen frame with a break of the Si–O–Me bond.

Earlier research established that with the RO : R<sub>2</sub>O ratio equal to 4.3–4.7, a low-shrinkage faience crock structure with good service properties is formed during the course of

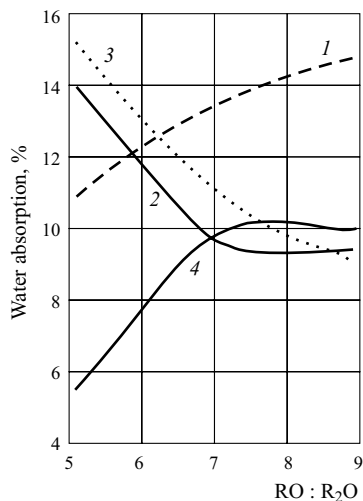
TABLE 1

Mixture	RO : R <sub>2</sub> O	Weight content, %			
		clay	sand	high-calcium waste	cullet
1	5	57.5	22.7	13.2	6.5
2	7	54.4	20.7	18.9	6.2
3	9	50.1	20.5	23.5	5.9

<sup>1</sup> South-Russian State Technical University, Novocherkassk, Russia.



**Fig. 1.** Water absorption  $W$ , fire shrinkage  $L$ , and compression strength  $\sigma_c$  versus RO : R<sub>2</sub>O ratio.

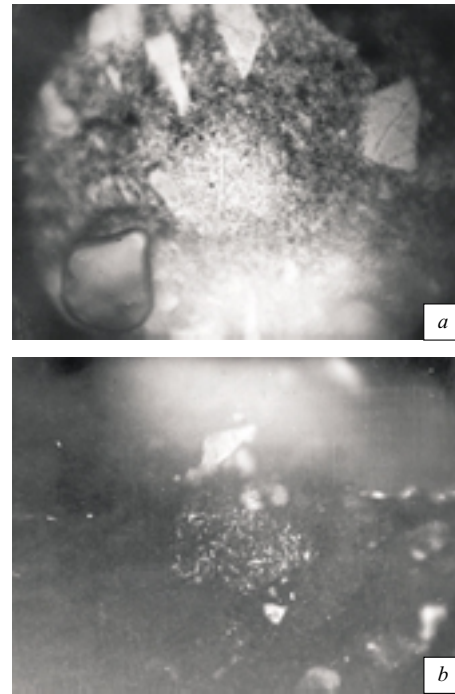


**Fig. 2.** Degree of ceramic crock sintering versus RO : R<sub>2</sub>O ratio: 1) without additive; 2, 3, and 4) with manganese ore additive of 5, 10, and 15%, respectively.

predominantly solid-phase sintering [3]. These investigations were continued, increasing the RO : R<sub>2</sub>O ratio from 5 to 9 due to an increased content of high-calcium waste (Table 1).

The ceramic mixtures were fired at 1000°C, after which the physicochemical properties of the samples were determined (Fig. 1).

The results of the study made it possible to identify a relationship between the physiochemical properties of the faience crock and the RO : R<sub>2</sub>O ratio and establish that the sintering processes in a mixture with RO : R<sub>2</sub>O = 5 significantly differ from similar processes in mixtures with RO : R<sub>2</sub>O = 7–9. An increase in the water absorption and shrinkage in the case of RO : R<sub>2</sub>O = 7–9 and the virtually constant mechanical strength (about 30 MPa), which is substantially lower than in samples with the ratio RO : R<sub>2</sub>O = 5, are presumably evidence of the growing role of solid-phase sintering in these samples and a decreased content of vitreous phase in the ceramics. The mechanical strength of the



**Fig. 3.** Structure of forming crystals ( $\times 320$ ) in direct (a) and polarized (b) light.

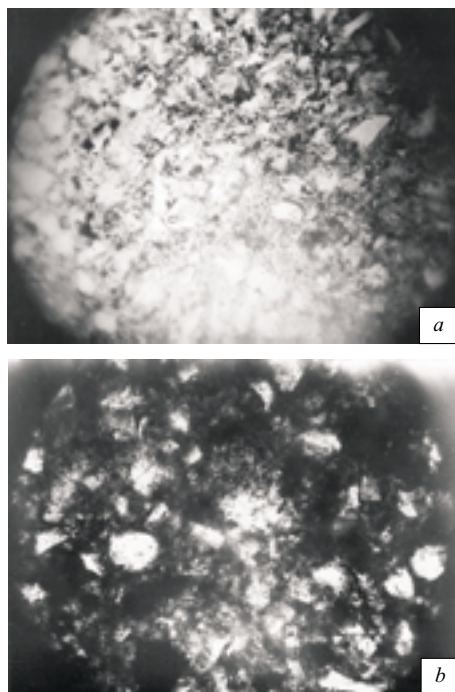
samples with RO : R<sub>2</sub>O = 5, which is equal to 50 MPa, is determined by the crock structure formation, in which an insignificant quantity of the vitreous phase binds the crystal grains. Thus, an increased calcium oxide content produced by using high-calcium waste results in the formation of a ceramic crock structure, different in its content of the crystalline and vitreous phases and its mineralogical composition, which is apparently determined by a different sintering mechanism.

Lithium and manganese oxides introduced in the form of Li<sub>2</sub>CO<sub>3</sub> and manganese ore were selected as intensifying additives to increase the amount of liquid phase.

Upon adding 1 to 2% Li<sub>2</sub>CO<sub>3</sub> to high-calcium mixtures, the sintering degree and the product strength increased by 10–20%. Manganese ore was introduced into high-calcium mixtures in the amounts of 5, 10, and 15%, for the purposes of tinting the mixture and intensifying the sintering process.

It was found that the shape of the curves reflecting the degree of sintering of materials significantly differs in the mixtures with different amounts of manganese ore. In the case of RO : R<sub>2</sub>O = 5, the water absorption of the samples with 5 and 10% manganese ore is higher than that of the samples without this ore, and the sintering degree is lower, whereas with the ratio RO : R<sub>2</sub>O = 7 and 9 and different quantities of manganese, the sintering process is intensified (Fig. 2)

The compression strength of the samples with different RO : R<sub>2</sub>O ratios has certain distinctions as well. Thus, with the ratio RO : R<sub>2</sub>O = 5 and the manganese ore content increasing from 5 to 15%, the strength remains virtually un-



**Fig. 4.** Large-crystalline crock structure ( $\times 280$ ) formed in the mixture with ratio  $RO : R_2O = 7 - 9$  (a) and ceramic crock structure ( $\times 280$ ) with manganese ore as a mineralizing additive (b).

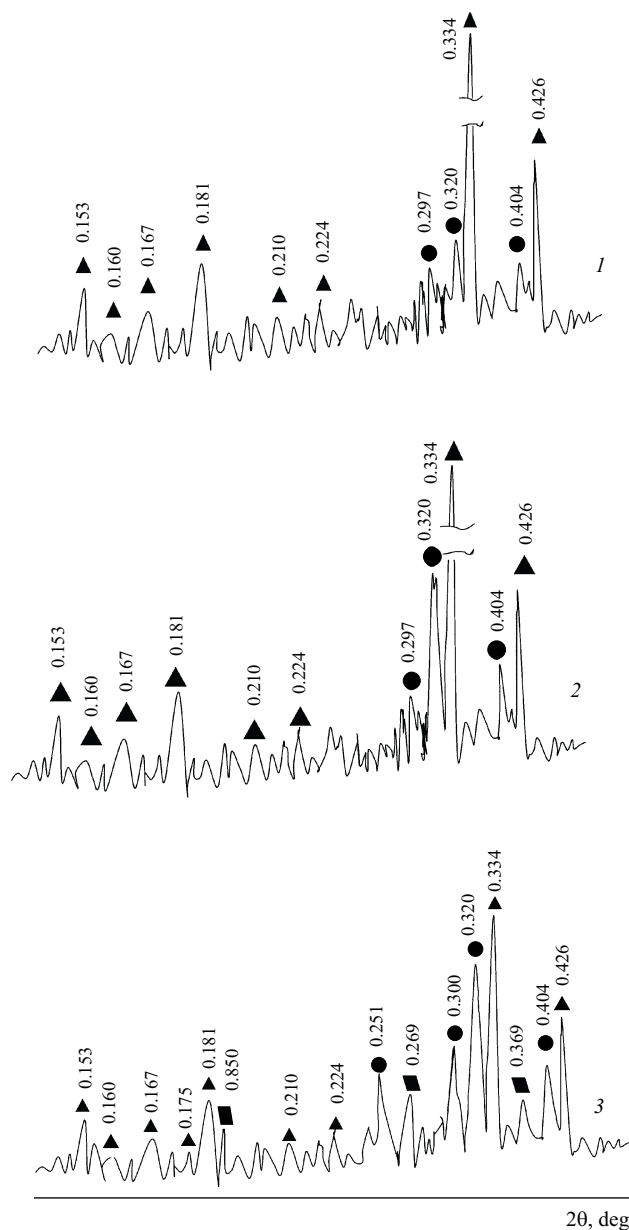
changed: 45 – 50 MPa, whereas with  $RO : R_2O = 7 - 9$ , the strength keeps increasing and amounts to 30 – 45 MPa.

The obtained data corroborated by physicochemical studies indicate that the sintering of calcium-bearing mixtures containing slime waste and mineralizers is intensified mainly in the solid-phase processes. The considered mixtures exhibited different types of sintering, and that is why intensification in them proceeded differently.

Petrographic studies established that with the ratio  $RO : R_2O = 5$ , a fine-crystalline structure of needle-shaped and prismatic microlytes is formed on vitreous phase sites (Fig. 3), whereas with  $RO : R_2O = 7 - 9$ , such sites are virtually absent, and a structure with larger crystals is formed, in which the newly formed crystals are also represented by single-phase needle and prismatic shapes (Fig. 4a). On adding 10% manganese ore, the crock structure with the ratio  $RO : R_2O = 7 - 9$  exhibits larger, more perfectly shaped, and uniformly distributed crystalline formations than the crock without additives, as well as dark-colored opaque isometrically shaped manganese oxide aggregates cemented by a dark brown compound in which microscopic crystalline formations can be observed (Fig. 4b) [4].

The x-ray phase analysis made it possible to determine the nature of the new formations and of the crystals introduced with the raw materials (Fig. 5). The main crystalline phase in the crock is anorthite  $CaO \cdot Al_2O_3 \cdot 2SiO_2$  (0.404, 0.297, and 0.251 nm) [5].

According to the petrographic data, the formed anorthite crystals are inhomogeneous in size, and consequently, the an-



**Fig. 5.** X-ray pattern of samples with  $RO : R_2O$  ratio equal to 7 – 9 (1), 5 (2), and 7 – 9 with manganese ore additive (3):  $\blacktriangle$  quartz;  $\blacktriangledown$   $(Ca, Mn)_2SiO_4$ ;  $\bullet$  anorthite.

orthite peaks on the x-ray patterns have various intensities. These data also suggest that the quantities of anorthite are different as well, which leads to the formation of the structures with different strength parameters (Table 1). In addition to this, the introduction of manganese ore into the mixtures with the ratio  $RO : R_2O = 7 - 9$  results in the formation of compounds of the  $(Mn, Ca)_2SiO_4$  type with interplanar distances of 0.269 and 0.369 nm. The formation of these compounds, whose densities are within the limit of  $3.49 \text{ g/cm}^3$ , along with anorthite makes it possible to produce ceramics with increased mechanical strength: up to 50 MPa.

It should be noted that when manganese ore is introduced to the mixture, the process of decarbonization and subse-

quent crystallization proceeds at temperatures 20 – 40°C lower than without manganese oxide participation. Furthermore, the tinting of calcium-bearing ceramic mixtures through the introduction of various quantities of manganese oxide modifies the crock color: from beige tints to dark gray color.

Thus, as the ratio  $RO : R_2O$  in a mixture with a high content of high-calcium waste grows, a large-crystalline structure is formed, in which anorthite is the main crystalline phase. The intensification of sintering in the mixtures with manganese ore additives is mainly observed in the solid-phase processes, with the formation of compounds of the  $(Mn, Ca)_2SiO_4$  type, which determines the increased strength of the ceramic material.

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